COMPLETE SPECIFICATION.

"METHOD OF PRODUCING A DISPERSION OF AN INORGANIC MATERIAL IN A FUEL OIL."

The following statement is a full description of this invention, including the best method of performing it known to us:-

This invention relates to processes for the incorporation of inorganic materials into fuel oils, particularly into high ash residual fuel oils.

The use of some fuel oils, particularly high ash residual fuel oils, in internal combustion power plants such as gas turbines, in furnaces and in other heating or power-raising appliances has hitherto suffered from certain disadvantages arising from the nature of, and the quantity of, the ash produced on combustion. While the nature of the ash from such fuel oils varies with the source of the petroleum from which they are derived, the ash always contains one or more metallic compounds which may possess properties detrimental to the materials with which the products of combustion come into contact. Thus the ash of such oils often contains vanadium or sodium compounds or both, and

these compounds can, under some conditions of combustion, cause corrosion or oxidation of metals, particularly under high temperature conditions. Even so-called heat-resistant metals, such as the nickel-chromium-iron alloys, may be subject to some deterioration when exposed to the combustion products of high ash residual fuel oils.

Also, the ash produced by the majority of high ash residual fuel oils has a comparatively low melting point and is liable to adhere to the surfaces with which it comes into contact, for example in a gas turbine plant to the turbine blades, thus giving rise to incrustations which may build up to such an extent that the efficiency of the power plant or furnace is adversely affected. The trend towards increased operating temperatures in modern power-raising plants has accentuated the difficulties arising from the detrimental properties of the ash produced on the combustion of residual fuel oils.

It has already been proposed to burn fuel oils in the presence of various inorganic compounds alleged to prevent the detrimental properties of fuel oil ash. Among the inorganic compounds suggested for this purpose are magnesium oxide, zinc oxide, barium carbonate, silica and some silicates, such as calcium and sodium silicates. Some of these inorganic compounds are alleged to form stable vanadates with the vanadium oxides in the fuel oil ash, and others are alleged to act merely by diluting the ash constituents with inert materials so that the harmful effects of such constituents are reduced.

Hitherto, the inorganic materials have been injected separately into the air supply lines or combustion chamber, or have been merely slurried with the fuel oil. In the latter case serious problems arise owing to the settling of the slurry and the resulting lack of homogeneity in the fuel feed to the burner. Based upon a recent discovery, the dispersion of inorganic colloids in fuel oils may be effected by mixing a hydrogel of an inorganic colloid with a fuel oil, separating the water from the resulting mixture and mechanically working the gel-oil system until the mixture is homogeneous. The present invention, however, provdies a simple and effective method for dispersing an inorganic material in a fuel oil, which results in a stable, homogeneous fuel oil composition and which does not necessitate converting the inorganic material into a hydrogel.

The present invention provides a method of producing

a dispersion of an inorganic material in a fuel il, which comprises mixing the said inorganic material with a fuel oil in th presence of an oil-soluble surface-active agent and mechanically working th resulting mixture until the product is substantially homogeneus.

The aforesaid techniqu enables inorganic materials t b dispersed in fuel ois to produce concentrates which can be bl nded easily into fuel oils at the refinery, can be added to the main fuel tank of an engine or furnace, or can be injected by a separate pump into the burner fuel line or air supply lines or combustion chamber of, for example, a gas turbine engine or a furnace.

While the method of the present invention may be applied to any fuel oil, it is of particular application to high ash residual fuel oils. Throughout this specification, the expression "high ash residual fuel oils" means liquid fuels having an ash content of at least 0.005% by weight when measured by method I. P. -4/ 44 (see "Standard Methods for Testing Petroleum and its Products", published by the Institute of Petroleum, 10th Edition, at pages 22 and 23) and a viscosity of a least 35 seconds Redwood I at 100°F and which consist of or contain a residual petroleum oil.

The high ash residual fuel oils with which this method is particularly concerned may consist wholly of residual petroleum oils or they may consist of mixtures of residual petroleum oils with other liquid fuels such as distilled or cracked hydrocarbon fuel oils. The invention is particularly useful in connection with high ash residual fuel oils which form on combustion an ash containing a major proportion of vanadium and/or sodium compounds.

The inorganic materials added to the fuel oils may be either synthetic materials or naturally-occurring materials, and include inorganic compounds of the elements of Groups 1, 11, 111, 1V and V111 of the Periodic Classification. Examples of suitable inorganic materials are silicon powder, inorganic oxides, such as silica, and inorganic oxides and hydroxides, such as those of magnesium, the alkaline earth metals, zinc, aluminium, c rium, zirconium, hafnium, thorium and iron.

Other inorganic materials which may be dispersed in fuel oils by means of the pr sent method include polyvalent metal carbonates such as those of magnesium, the alkaline earth met-

als, zinc and iron; silicates such as those of sodium, magnesium, the alkaline earth metals and aluminium; various polyvalent metal sulphides such as ferrous sulphide and cuprous sulphide; various metallic aluminates, sulphates and phosphates; various carbides such as those of calcium, aluminium and silicon; various silicides such as calcium silicide; compounds of lead; compounds of the Rare Earth elements; and various alloy powders such as ferr s-ilicon. Synthetic zeolites such as the magnesium silicates and the aluminium silicates may also be employed.

The naturally occurring materials which may be em-ployed include the naturally occurring forms of the compounds specified above, or mixtures of such compounds, and are exem-plified by kieselguhr, talc, asbestine, and materials of a clay-like nature such as the swelling type bentonite clays and the non-sw lling clays such as Georgia Kaolinite. Magnesium mont-morillonites, such as Hectorite, and Wyoming montmorillonites, ordinarily regarded as aluminium montmorillonites are also suitable additives.

Mixtures of inorganic materials, such as mixtures of the compounds specified above, may be employed in this method.

The oil-soluble surface-active agent employed in the method according to the present invention may be a cationic, anionic or non-ionic surface-active agent. Typical oil-soluble surface-active agents which may be employed are long-chain amines, metal soaps, such as those of aluminium and zinc, sul-phonated fatty oils, sulphonated mineral oils, and lecithin and other oil-soluble organic phosphorus compounds.

A preferred class of surface-active agents is the oil-soluble cationic surface-active agents such as amino compounds having at least 8 carbon atoms in the molecule and especially the oleophilic quaternary ammonium compounds. The quater-nary ammonium compounds which have been found to be expeci-ally effective are those which contain at least one and preferably two aliphatic hydrocarbon chains of 8 or more carbon atoms, such as trimethyl octadecyl ammonium chloride, trimethyl octa-decadienyl ammonium chloride, trimethyl hexadecyl ammonium chloride, trimethyl tetradecyl ammonium chloride, trimethyl octadecenyl ammonium chloride, dimethyl dioctadecyl ammon-ium chloride, dimethyl dihexadecyl ammonium chloride, di-methyl di-tetradecyl ammonium chloride, dimethyl octadecyl octadecenyl ammonium chloride, dimethyl octadecenyl octadec-

adienyl ammonium chloride, diethyl dih xadecyl ammonium chl r-
ide and ethyl propyl dioctadecyl ammonium chloride. While
the quaternary ammonium chlorides hav been ex mplified above,
the corresponding bromides, acetates or hydroxides may be em-
ployed. It will be further understood that the short-chain rad-
icals present in each of the above-designated quaternary salts
r more or less immaterial, but may be preferably aliphatic
radicals having from 1 to 7 carbon atoms. Mixtures of these
quaternary ammonium compounds may also be used. Commer-
cially available quaternary salts of the above variety are usually
materials wherein the long-chain radicals have from 12 to 18 12 r 18
carbon atoms each.

Suitable oil-soluble surface-active agents also include the
alkyl amines having at least 8 carbon atoms, and preferably from
12 to 24 carbon atoms, in the molecule, as well as oil-soluble
salts thereof such as their acetates. Preferably, these are
primary or secondary amines such as dodecylamine, heptadecy-
lamine and octadecylamine. Cyclic amines may be employed
in the present process and include especially the alkylated imi-
dazolines, such as heptadecyl imidazoline, the alkylated pyrimi-
dines, substituted acridines, benzidine, and diphenylamine.
Other surface-active agents which have been found to be useful
include oil-soluble partial amides of alkylene diamines or of
polyalkylene polyamines or oil-soluble salts of such partial amid-
es. Typical examples are oleyl-amidoethylamine oleate and
aminoethyl stearamide. Complex polyamino compounds also
useful in the present method include the amines obtained by the
chlorination and subsequent ammonolysis of paraffin wax, the
higher fatty acid salts of polyamines derived from the interaction
of acrolein and ammonia and the adducts of hydrogen sulphide
and diallyl amine.

A special variety of complex polyamines which may be
employed comprises those containing both hydroxy and amino
radicals obtained, for example, by the action of ethylene oxide
or ethylene glycol on polyethylene polyamines or by condensation
of epihalohydrins with ammonia or amino compounds. The latter
condensation products especially after partial amide formation
with high molecular weight carboxylic acids, particularly those
having at least seven carb n atoms in the molecule, have been
found to be especially effective in the present method.

Th ammonia- pichlorhydrin condensation products may

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be mixed with an oleophilic acid, or mixtures ther of, such as tall oil or higher fatty acids d rived from animal or v getable oils or the partial oxidation products of hydrocarbon mixtures such as various petroleum fractions, and the mixture heated at a temperature from about 150° to about 225°C for a period of from about 15 minutes to about two hours, or longer if desired, wher - by the ammonia-epichlorhydrin product is converted to an amide especially effective in the present invention. Representative of fatty acids suitable for the production of these amides ar lauric, oleic, linoleic, palmitic, stearic, and carnaubic acid. Various naphthenic acids recoverable from petroleum fractions may be used, as well as resin acids such as abietic acid and pimaric acid, and other cyclic acids such as salicylic acid and alkyl sali-cylic acids. Acid mixtures such as may be obtained from oxidized waxes, coconut fat, wool fat, castor oil, and th like, are also well adapted for use in the preparation of these oil-soluble surface-active agents.

Further oil-soluble surface-active agents useful in the present invention include the oleophilic soaps of carboxylic and organic sulphonic acids. A preferred group of this type is the polyvalent metal salts and particularly the amphoteric metal salts of carboxylic acids, especially those wherein the carboxylic acids are fatty acids having at least 12 carbon atoms in th molecule. Other types of acids forming suitable soaps includ petroleum naphthenic acids, acids derived from animal, plant and fish oils, rosin acids and tall oil acids. Specific examples are aluminium stearate, the aluminium salt of 12-hydroxy stearic acid, calcium naphthenate and zinc stearate. Monovalent metal soaps such as the alkali metal soaps of petroleum sulphonic acids, e.g. the sodium petroleum sulphonates, or of sulphosuccinic acids such as the sodium soap of sulpho di-iso-octyl succinic acid, may also be employed.

Especially when amphoteric or basic inorganic materials are dispersed in fuel oils, acidic oil-soluble surface-active agents may be used. Preferably these are the higher molecular weight organic acids, such as carboxylic, sulphinic and sulphonic acids, having 12 or more carbon atoms in the molecule. Typical examples of such acids are stearic acid, linoleic acid, tetradec-ane-1-sulphonic acid, dodecane-1-sulphonic acid, and the pro-ducts resulting from the sulphonation of fatty oils or mineral oils, such as the petroleum sulphonic acids. Hydroxy fatty acids,

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such as 12-hydroxystearic acid, are also effective.

Further surface-active agents effective in the present method are th non-ionic surfac -activ agents, such as th oil-soluble hydroxyl-containing organic compounds, for example the oil-soluble glycols, partially hydrolysed glycerides, high molecular weight monohydric alcohols, and condensation products of ethylene or propylene glycol with alcohols or carboxylic acids. Typical examples of such compounds are glycerol monostearat , hydrongenated castor oil, cetyl alcohol, 1,10-decamethylen glycol and the condensation products of ethylene oxide with naphthenic acids.

Numerous organic compounds containing phosphorus may be employed as oil-soluble surface-active agents in this method. Examples thereof include the partial esters of various phosphoric acids, expecially orthophosphoric acid, and the phosphonic acids. Blown or oxidized fatty oils which have been phosphated with phosphoric acid to form oil-soluble surface-active agents, and the lecithins which are salts of naturally occurring phosphoric esters with choline are examples of the phosphorus compounds which may be used.

The amount of the oil-soluble surface-active agent that may be employed in the present method varies between 0.1% and 20%, and preferably between 0.5% and 3.0% by weight, based on th weight of inorganic material present in the mixture.

Mechanical working of the mixture comprising the inorganic material, the oil-soluble surface-active agent and the fuel oil is an important feature of the method of the present invention, for without such mechanical working unstable products are formed which separate gritty aggregates of inorganic material on standing. Any suitable dispersing, shearing or pulverizing apparatus may be used for rendering the mixture of the crushed or powd r d inorganic material, the oil-soluble surface-active agent and the fu 1 oil substantially homogeneous. Such apparatus includes a paint mill such as a triple roll mill, an edge runner or a ball mill, or a colloid mill such as a high pressure pump, providing at least a pressure of 5000 pounds per square inch, which forces the mixture through orifices of small diameter.

The inorganic material, the oil-soluble surface-active agent and the fu 1 oil may be mixed together in on operation or may be mixed in stages. In the former case, quantities of the inorganic additive, the oil-soluble surface-active agent and the

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fuel oil are stirred together and th resulting slurry is mechan-
ically worked by passing the slurry through a dispersing appara-
tus one or more times until the product is substantially homo-
geneous. In the latter case, a mixture of the inorganic material
and a sample of the fuel oil is mechanically worked by passing
it through a dispersing apparatus one or more times, and to the
resulting paste is added a mixture of the oil-soluble surface-
active agent dissolved in a further sample of the fuel oil. The
mixture so formed is then mechanically worked by passing it
through a dispersing apparatus one or more times until the prod-
uct is substantially homogeneous.

In an alternative manner of carrying out the present
method, one portion of the oil-soluble surface-active agent is
added to the fuel oil and another portion to the inorganic material.
Both mixtures are then mechanically worked either by stirring
or by passing through a dispersing apparatus one or more times,
the two mixtures are then combined, and the resulting mixture
is passed through a dispersing apparatus one or more times until
the product is substantially homogeneous.

A further alternative comprises the addition of reagents
capable of forming an oil-soluble, surface-active agent separa-
tely to the inorganic material and to the fuel oil. An example
of this consists of incorporating an amine as an emulsion in the
inorganic material and the separate incorporation of a fatty acid
containing at least 7 carbon atoms in the molecule in the oil.
When these two mixtures are mixed and subsequently heated,
the amine and the acid react to form a mixture of amine salts
and amides which act as an oil-soluble surface-active agent
during the subsequent mechanical working.

The mechanical working may be conducted at ambient
or elevated temperatures, for example between 15°C and 180°C,
depending on the viscosity of the fuel oil.

Fuel oil concentrates prepared by the method of this
invention may contain from 1% to 70% of the inorganic material,
and preferably from 10% to 65% by weight. These concentrates
may be used for the production of fuel oils containing the inorgan-
ic material in an amount of from 0.01% to 0.5% by weight by
dilution with the appropriate amount of fuel oil by any suitable
stirring procedure. An example of a very suitable concentrate
is one containing 60% by weight of silica in a fuel oil having a
viscosity of 900 seconds Redwood 1 at 140°F. When prepared

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by the present methods, such concentrates do not separate the inorganic material during storage. The method of the present inventi n is illustrated by the following Examples:

EXAMPLE 1.

40 parts by weight of silica of particle size ranging from 2 t 5 microns were stirred into 16 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. The mixture was then thoroughly dispersed by two passes through a steel triple roll mill.

1 part by weight of aluminium stearate was added to 10 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. the mixture was heated to 140°C and was stirred until the aluminium stearate dissolved. The mixture was allowed to cool. It formed a gel at room temperature.

4.4 parts by weight of the gel were dispersed in the silica paste prepared as above by passing the mixture of the gel and silica paste once through a steel triple roll mill. The resultant paste contained 1% by weight of aluminium stearate based on the silica content of the paste.

A sample of the concentrate prepared as hereinbefore described was diluted with a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F to give a fuel oil containing approximately 0.25% of silica. No settling occurred after the product had been stored for seven days at room temperature.

EXAMPLE 11.

40 parts by weight of powdered asbestine, an inorganic material consisting of magnesium aluminium silicate, were stirred into 26 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. The mixture was then thoroughly dispersed by two passes through a triple roll mill.

1 part by weight of aluminium stearate was added to 10 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F, the mixture was heated to 140°C and was stirred until the aluminium stearate dissolved. The mixture was allowed to cool. It formed a gel at room temperature.

4.4 parts by weight of the gel were dispersed in the asbestine paste prepared as above by passing the mixture of the gel and asb stine paste once through a steel triple roll mill. The resultant paste contained 1% by weight of aluminium stearate

based on the asbestine content of the paste.

A sample of the concentrate pr par d as hereinbefore described was diluted with a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F to give a fuel oil containing approximately 0.05% of asbestine. No settling occurred after the product had been stored for seven days at room temperature.

EXAMPLE 111.

100 parts by weight of powdered asbestine were stirred into 60 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. The mixture was then thoroughly dispersed by two passes through a roll mill.

1 part by weight of an oil-soluble surface-active agent marketed under the trade name Aerosol OT was added to 9 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. Aerosol OT is sodium sulpho di-iso-octyl succinate. The mixture was heated to 100°C, was stirred until the Aerosol OT dissolved and was then allowed to cool.

The solution of the Aerosol OT was added to the asbestine paste prepared as above and passed once through a steel triple roll mill. A sample of the resulting concentrate was diluted with a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F to give a fuel oil containing approximately 0.2% of asbestine. The product was heated at 100°C for 24 hours, and was allowed to stand for four days at ambient temperatures. No settling occurred therein.

EXAMPLE IV.

100 parts by weight of finely divided magnesium carbonate were stirred into 400 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F. The mixture was then thoroughly dispersed by two passes through a steel triple roll mill.

1 part by weight of aluminium stearate was added to 9 parts by weight of a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F, the mixture was heated to 140°C and was stirred until the aluminium stearate dissolved. The mixture was allowed to cool. It formed a gel at room temperature.

The gel was added to the mixture of magnesium carbonate and fuel oil prepared as above and the resulting mixture passed through a steel triple roll mill.

A sample of the resulting concentrate was diluted with a fuel oil having a viscosity of 2000 seconds Redwood 1 at 140°F to giv a fuel oil containing approximately 0.2% of magnesium carbonate. No settling occurred after the product had been heated at 100°C for 24 hours.

The claims defining the invention are as follows:

1. A method of producing a dispersion of an inorganic material in a fuel oil, which comprises mixing the said inorganic material with a fuel oil in the presence of an oil-soluble surface-active agent and mechanically working the resulting mixture until the product is substantially homogeneous. (16th November, 1953)

2. A method as claimed in claim 1, wherein the mechanical working is conducted at a temperature between 15°C and 180°C. (16th November, 1953)

3. A method as claimed in claim 1 or 2, wherein the inorganic material is an inorganic compound of an element of Group 1, 11, 111, 1V or V11 of the Periodic Classification. (16th November, 1953)

4. A method as claimed in any one of the preceding claims, wherein the inorganic material is an inorganic oxide or hydroxide. (16th November, 1953)

5. A method as claimed in claim 4, wherein the inorganic material is an oxide or hydroxide of magnesium, an alkaline earth metal, zinc, aluminium, cerium, zirconium, hafnium, thorium or iron. (16th November, 1953)

6. A method as claimed in any one of claims 1 to 3, wherein the inorganic material is a carbonate of a polyvalent metal. (16th November, 1953)

7. A method as claimed in claim 6, wherein the inorganic material is a carbonate of magnesium, an alkaline earth metal, zinc or iron. (16th November, 1953)

8. A method as claimed in any one of claims 1 to 3, wherein the inorganic material is a metallic phosphate.

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(16th November, 1953)

9. A method as claimed in any one of claims 1 to 3, wherein the inorganic material is a silicate of sodium, magnesium, an alkaline earth metal or aluminium. (16th November, 1953)

10. A method as claimed in claim 9, wherein the silicate is talc or asbestine. (16th November, 1953)

11. A method as claimed in claim 9, wherein the silicate is a clay. (16th November, 1953)

12. A method as claimed in claim 4, wherein the inorganic material is silica. (16th November, 1953)

13. A method as claimed in any one of the preceding claims, wherein the fuel oil is a high ash residual fuel oil as hereinbefore defined. (16th November, 1953)

14. A method as claimed in claim 13, wherein the high ash residual fuel oil forms on combustion an ash containing a major proportion of vanadium and/or sodium compounds. (16th November, 1953)

15. A method as claimed in claim 13 or 14, wherein the residual fuel oil is a mixture of residual petroleum oils with distilled or cracked hydrocarbon fuel oils. (16th November, 1953)

16. A method as claimed in any one of the preceding claims, wherein the oil-soluble, surface-active agent is an oil-soluble cationic surface-active agent. (16th November, 1953)

17. A method as claimed in claim 16, wherein the surface-active agent is an alkyl amine having at least eight carbon atoms in the molecule or an oil-soluble salt thereof. (16th November, 1953)

18. A method as claimed in claim 16, wherein the surface-active agent is a quaternary ammonium compound having at least one aliphatic hydrocarbon chain of eight or more carbon atoms. (16th November, 1953)

19. A method as claimed in claim 16, wherein the sur-face-activ agent is a polyamine containing both hydroxy and amino radicals or a partial amide thereof with a high molecular weight carboxylic acid. (16th November, 1953)

20. A method as claimed in claim 16, wherein the sur-face-active agent is a partial amide of a polyalkylene polyamine. (16th November, 1953)

21. A method as claimed in any one of claimes 1 to 15, wherein the surface-active agent is a polyvalent metal salt of a fatty acid having at least 12 carbon atoms in the molecule. (16th November, 1953)

22. A method as claimed in claim 21, wherein the poly-valent metal is aluminium or zinc. (16th November, 1953)

23. A method as claimed in any one of claims 1 to 15, wherein the surface-active agent is an organic acid having at least twelve carbon atoms in the molecule. (16th November, 1953)

24. A method as claimed in any one of the preceding claims, wherein the surface-active agent is present in an amount between 0.1% and 20% of the weight of the inorganic material present in the mixture. (16th November, 1953)

25. A method as claimed in any one of the preceding claims, wherein the inorganic material, the oil-soluble surface-active agent and the fuel oil are mixed in stages. (16th Nov mber 1953)

26. A method as claimed in any one of the preceding claims, wherein the mechanical working is achieved by means of a shearing or pulverizing apparatus. (16th November, 1953)

27. A method as claimed in any one of the preceding claims, wherein the mechanical working is achieved by means of a roll mill, edge runner, ball mill or colloid mill. (16th November, 1953)

28. A method as claimed in any one of the preceding claims, wherein the ingredients are used in such proportions as to yield a fuel oil concentrate containing from 1% to 70% by weight of the inorganic material. (16th November, 1953)

29. A method as claimed in any one of the preceding claims, wherein the resulting dispersion is diluted with fuel oil to produce fuel oils containing the inorganic material in an amount of from 0.01% to 0.5% by weight. (16th November, 1953)

30. Methods for the production of dispersions of an inorganic material in fuel oil substantially as hereinbefore described with particular reference to Examples 1 and 11. (16th November, 1953)

31. Dispersions of inorganic materials in fuel oils whenever prepared in accordance with any one of the preceding claims. (16th November, 1953)

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FORMATION AND PROPERTIES OF CHELATED ALUMI-NUMALKOXIDES

R. Naß and H. Schmidt

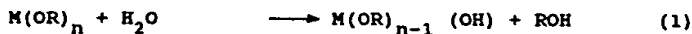Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-8700 Würzburg, Federal Republic of Germany

ABSTRACT

Chelated aluminumalkoxides have been prepared from the re-
action of aluminum-secbutoxide with acetylacetone (AcAc)
or ethylacetoacetate (EAA) in different alkoxide/chelating
agent molar ratios. These compounds have been used to
study the possibility of controlling the rate of hydroly-
sis of aluminumalkoxides and/or the polycondensation of
the related hydroxides. Hydrolysis was followed by NIR-
spectroscopy and showed no differences for chelated alumi-
num-secbutoxide and the pure alkoxide. In contrast the po-
lycondensation of aluminumhydroxides chelated with ethyl-
acetoacetate decreased remarkably and depends on the alk-
oxide/chelating agent molar ratio. The properties of these
aluminum hydroxides have been studied by different methods
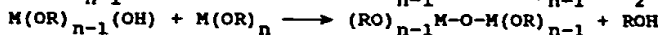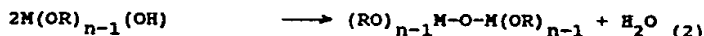and a structural model for $Al(OH)_2EAA$ has been evaluated.

INTRODUCTION

Sol-gel processing for the preparation of glass, glass ce-
ramics, and ceramics has been studied intensively during
the last few years. A survey over the literature shows
that most of the elaborated synthesis for these different
materials involve the use of molecular precursors, mainly
metal alkoxides, as the starting material. The macromo-
lecular, inorganic network is then obtained by hydrolysis
and polycondensation, which may be written as follows
(eqs. 1 and 2):

Hydrolysis

$$M(OR)_n + H_2O \longrightarrow M(OR)_{n-1}(OH) + ROH \qquad (1)$$

Polycondensation

$$2M(OR)_{n-1}(OH) \longrightarrow (RO)_{n-1}M-O-M(OR)_{n-1} + H_2O \qquad (2)$$
$$M(OR)_{n-1}(OH) + M(OR)_n \longrightarrow (RO)_{n-1}M-O-M(OR)_{n-1} + ROH$$

To a great deal, the properties of the final product de-
pend on the competitive/complementary rates of these two
reactions, as it has already been shown for the prepara-
tion of silica from alkoxysilanes [1]. For tailoring the
properties of the final product a good knowledge of the
kinetic of these reactions is necessary as well as the de-

velopment of methods for reaction control. In the present
paper we report first results about reaction control for
the preparation of alumina by chemical modification of
aluminum-secbutoxide with ß-dicarbonyl compounds.

EXPERIMENTAL

A solution of aluminum-secbutoxide, $Al(OBu^s)_3$ in iso-pro-
panol (2 mol/l) has been reacted with acetylacetone (AcAc)
or ethylacetoacetate (EAA) in different molar ratios, giv-
ing clear solutions. The modified precursor was hydrolysed
with stoichiometric quantities of water in relation to the
number of hydrolysable OBu^s-groups. The experimental pro-
cedure is shown in detail in figure 1 and the reaction
conditions along with the experimental observations during
hydrolysis are summarized in table 1. Clear solutions or
sols were studied by FTIR spectroscopy using a circle cell
with a ZnSe-crystal and gel-powders were measured using
kBr pellets.
Dynamic light scattering experiments were performed with
freshly prepared sols (E1, E2) using a Malvern 4700.
The chemical composition of the sample E1 was determined
by C, H analysis and the aluminum content was determined
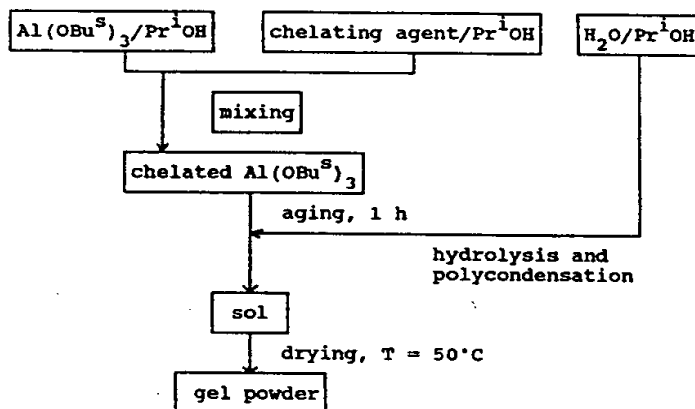as $\alpha\text{-Al}_2O_3$.

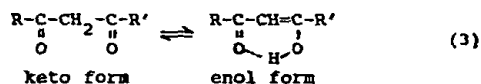Figure 1: Flow chart for the preparation of chelated
aluminumhydroxides

Table 1. Reaction conditions and experimental observations
for the preparation of chelated aluminum-
hydroxides

Sample no.	chelating agent (Lig)	molar ratio Al(OBu^s)$_3$/Lig	(OBu^s)/Lig	product after hydrolysis
A1		1	2	precipitate
A2	AcAc	2	2	precipitate
A3		3	2.75	precipitate
E1		1	2	clear sol.
E2	EAA	2	2.5	clear sol.
E3		3	2.75	precipitate

RESULTS AND DISCUSSION
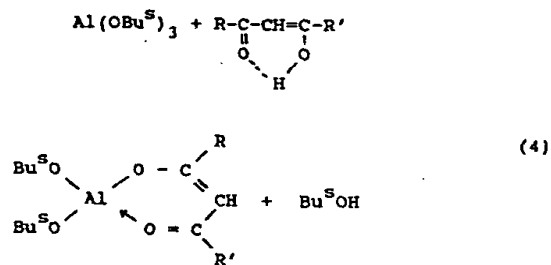
Chelation

Acetylacetone and ethylacetoacetate are both ß-dicarbonyl
compounds and therefore exhibit keto-enol-tautomerism
(eq. 3).

$$R\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}R' \rightleftharpoons R\text{-}\underset{O_{\diagdown H\diagup}O}{\underset{\|}{C}}\text{-}CH=C\text{-}R' \qquad (3)$$

keto form   enol form

R,R': CH$_3$ (AcAc)
R: CH$_3$, R': OC$_2$H$_5$ (EAA)

The chelating properties of these compounds are due to the
presence of a reactive hydroxyl group in the enol form
which reacts like an acid. The amount of present enol
strongly depends on the nature of the groups R and R'. In
the case of AcAc (R,R': CH$_3$) according to [2] the enolic
content is about 76.4 % whereas the enolic content of EAA
(R: CH$_3$, R': OC$_2$H$_5$) is only about 8 %. These differences
have to be taken into account for the reaction of
Al(OBu^s)$_3$ with one of these chelating agents, because the
time required to complete chelation may be rather diffe-
rent for different R and R'. For this reason the solutions
were aged for 1 hour after mixing to be sure that chela-
tion was complete to the greatest possible extent. How-
ever, the reaction of AcAc and EAA, respectively, with
Al(OBu^s)$_3$ can be written as follows (eq. 4):

$$Al(OBu^S)_3 + R-C-CH=C-R'$$

with the structure showing the carbonyl/enol:

$$
\underset{O\diagdown_{}O}{\overset{\parallel}{}}\underset{H}{}
$$

$$
Bu^SO\diagdown O-C\diagup R (4)
$$
$$
Al \diagdown\diagup CH + Bu^SOH
$$
$$
Bu^SO\diagup O=C\diagdown R'
$$

The reactive enol form of the β-dicarbonyl compound substitutes a OBu^S-group of $Al(OBu^S)_3$ giving a structure where the anion of the chelating agent is stabilized by chelating the aluminum atom. The formation of chelated species has been *confirmed by* FTIR-spectroscopy of the solution. Both β-dicarbonyl compounds exhibit strong carbonyl *stretching vibrations between* $1710\ cm^{-1}$ and $1610\ cm^{-1}$ in a solution of iso-propanol. These vibrations are shifted to lower wavenumbers ($1620\ cm^{-1}$, $1520\ cm^{-1}$) after the reaction, typical for complexes of AcAc and EAA, respectively [3].

It is quite important to note that β-dicarbonyl compound substitutes alkoxygroups in $Al(OBu^S)_3$ and therefore changes the functionality of the precursor. This provides a possibility to fix the type of network formed lateron through hydrolysis and polycondensation on a molecular level depending only on the molar alkoxide/chelating agent ratio. For example if the molar ratio is equal to one (A1, E1) a two dimensional structure can be formed only, whereas molar ratios greater than one should lead to a well defined mixture of two- and threedimensional crosslinking. This principle has already been applied successfully to the preparation of alumina fibres from $Al(OBu^S)_3$, EAA and H_2O [4].

Hydrolysis

Hydrolysis was performed with stoichiometric quantities of water with regard to the different molar $Al(OBu^S)_3$/chelating agent ratios. The behaviour of the precursors depends on the nature of the chelating agent and the molar ratios of the reactants (table 1). Immediately after the addition of the water/iso-propanol solution precipitates were formed, except the samples E1 and E2.

The appearance of precipitates makes it impossible to study the hydrolysis behaviour of the different precursors (A1 - A3, E3) in solution by FTIR and NIR spectroscopy. However, the formation of precipitates is very similar to the hydrolysis of pure $Al(OBu^S)_3$. In this case the addition of water to an alkoholic solution of $Al(OBu^S)_3$ yields to a gelatinous precipitate at once and this behaviour can be interpreted as a fast hydrolysis and condensation. For

E1 and E2 which form clear sols after hydrolysis, NIR
spectroscopy was chosen for the H_2O analysis because water
exhibits a distinct absorption around 1940 nm which is not
influenced by vibrations of the other compounds in the so-
lution.
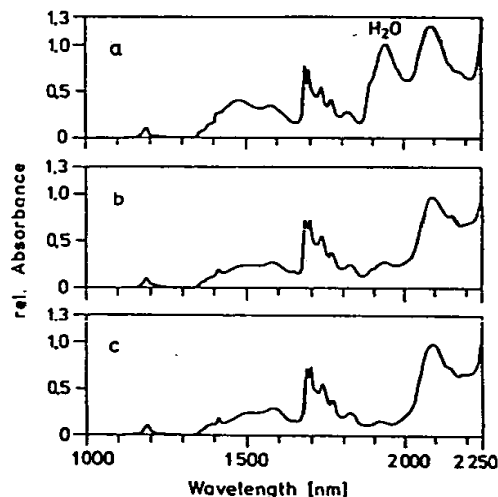The results of these experiments are shown in fig. 2 for
the systems E1.

Figure 2. NIR-spectra of the system E1 and the H_2O/Pr^iOH
solution
a) H_2O/Pr^iOH solution
b) sample after hydrolysis
(reaction time 1 minute)
c) unhydrolyzed sample

Water exhibits a distinct, intensive absorption around
1940 nm in the H_2O/Pr^iOH solution (fig. 2a) which was used
to perform the hydrolysis of the chelated alkoxide (fig.
2c). The absorption at 1940 nm should decrease slowly af-
ter mixing the reactants, if the rate of hydrolysis is
significantly influenced by the chelating agent. Fig. 2b
shows a NIR spectrum after a reaction time of 1 minute. It
is obvious that no water can be detected in this spectrum.
This result must be explained in a way that hydrolysis is
complete even after a reaction time of one minute and
therefore the rate of hydrolysis of the chelated alkoxide
(E1) cannot be very different from that of the pure
$Al(OBu^s)_3$. The same results were obtained for the system
E2 and therefore one must assume that the hydrolysis of
$Al(OBu^s)_3$ is not influenced by chelation with ß-dicarbonyl
compounds.

The nature of the aluminumhydroxides formed during hydrolysis of the chelated $Al(OBu^s)_3$ was studied by FTIR spectroscopy and the formation of chelated aluminumhydroxides would be proved by this method. In all cases the presence of the chelating agents (AcAc, EAA) was indicated by the strong carbonyl stretching vibrations around 1620 cm^{-1} and 1520 cm^{-1}, whereas the hydroxyl groups bonded to alumina gave intensive absorptions around 3600 cm^{-1}.
Furthermore, no hint of advice could be found for the hydrolysis of the chelating agent. These results agree with the partial charge model developed by Livage and Sanchez [5]. Following this model alkoxy groups are preferentially hydrolysed in comparison to chelating agents like AcAc and EAA, respectively.

Polycondensation

The extent of polycondensation was determined indirectly by dynamic light scattering experiments on freshly prepared sols and solubility tests with gel-powders for the samples E1 and E2, respectively. The results are summarized in table 2.

Table 2. Properties of chelated aluminumhydroxides

Sample no.	size of sol particles [nm]	solubility of gel powder in toluene $[g \cdot cm^{-3}]$	
E1	1.2 - 2.5	≈1	clear solution
E2	2.3 - 4.7	≈0.8	translucent

The size of the sol particles depends on the molar $Al(OBu^s)_3$/EAA ratio and with a decreasing quantity of EAA the particle size increases. However, the particles are smaller than 5 nm and for this reason polycondensation has taken place only to a very limited extent. Furthermore, the rate of condensation seems to be rather slow at room temperature because the sols do not gel after aging for more than 3 months. Similar results have recently been reported for the preparation of titania from titanium tetraethoxide and AcAc [6]. In this system the particle diameter is around 50 nm and this fact has been explained in terms of a low degree of condensation. In the case of alumina this assumption was proved for the sample E1 because the good solubility of the gel powder in toluene makes it ideal for further studies. The chemical composition of the gel powder was determined by chemical analysis which fit the formula $Al(OH)_2EAA$ as expected from the reactant ratios. The molecular weight of the molecules in solution was studied by vapor pressure osmometry. This method gave an average of 940 g/mol as molecular weight and in view of the fact that the molecular weight of $Al(OH)_2EAA$ is 190 g/mol a pentameric compound $[Al(OH)_2EAA]_5$ can be assumed.

In order to get more information about the structure and
the coordination of the aluminum in this oligomer, the so-
lution was studied by ^{27}Al-NMR-spectroscopy. This method
is quite suitable to determine the coordination number of
aluminum atoms, because the chemical shift of four-fold
coordination is quite different from that of a six-fold
coordinated aluminum [7]. A typical ^{27}Al-NMR-spectrum of
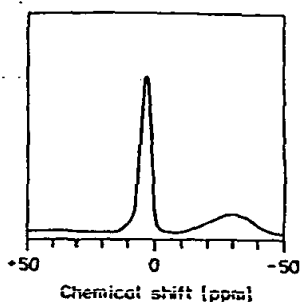Al(OH)$_2$EAA is shown in figure 3.

Figure 3: ^{27}Al-NMR-spectrum of Al(OH)$_2$EAA

The ^{27}Al-NMR-spectrum shows one sharp intensive peak cen-
tered at +3,5 ppm and a second broad peak of lower inten-
sity around - 26,6 ppm. The shape and chemical shift of
the first peak is typical for a six-fold coordinated alu-
minum atom whereas the broad peak is due to a coordination
number of four. On the basis of these data a model for the
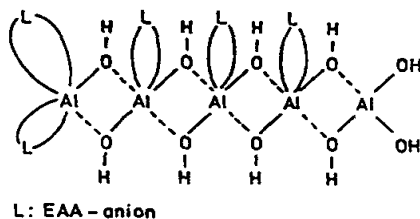structure of [Al(OH)$_2$EAA]$_5$ can be supposed which is shown
in figure 4.

L: EAA - anion

Figure 4: Model for the structure of [Al(OH)$_2$EAA]$_5$

This model is based on the NMR data and the assumption
that a five-fold coordination state is an unfavorable one.
Therefore, for the five membered species it becomes neces-
sary that that one six-fold coordinated Al atoms caries
two ligands and another one remains in the four-fold coor-
dinated uncomplexed state (according to fig. 4).

A similar behaviour has been described previously by Williams and Interrante for the reaction of aluminum-iso-propoxide and AcAc on the basis of a structural analysis [8] which supports our model. Nevertheless, these results show that polycondensation may be controlled by the use of ß-dicarbonyl compound.

CONCLUSIONS

New precursors for the preparation of alumina via the sol-gel process can be prepared from aluminumalkoxides and ß-dicarbonyl compounds. The main advantages of these precursors are:
- The preparation of aluminumhydroxides which are soluble in organic solvents like toluene is possible.
- Polycondensation can be completely suppressed and therefore very small sol particles (< 5 nm) can be prepared.
- Chelating agents with reactive organic groups can be used and give the possibility to prepare completely new inorganic-organic materials.

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